

***In situ* and *operando* investigation of the reactivity of C₃N₄-supported Ni and Cu single-atom catalysts during hydrogenation**

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Highlights

- In-depth reactivity study of C₃N₄-supported SACs in advanced *in situ* techniques.
- Successful synthesis and characterization of Ni- and Cu-containing single-atom catalysts on C₃N₄.
- *Operando* XAS investigation reveals conditions leading to metal aggregation in hydrogenation.
- Quantitative insights into metal aggregation impact, highlighting oxidation state and coordination changes.

1. Introduction

Single-atom catalysts (SACs) are catalysts in which the active metal species exist as atomically-dispersed atoms entrapped within a catalytically inactive support, generally carbon-based or oxidic.¹ The metal element, its oxidation states, its coordinative environment within the active site, and the chosen support material affect to some extent the activity, stability and selectivity of these catalysts, and are responsible for their excellent activity, selectivity, and stability, and the possibility for applications in several chemical reactions, including, among others, selective hydrogenation, cyclization, hydrogen evolution and CO₂ reduction reactions.² Our group has played a key role in the development of the first stable single-atom catalyst on carbon matrices.³ However, despite these breakthroughs, an in-depth and detailed characterization of the reactivity of SACs supported on carbon nitride (C₃N₄), and an in-depth understanding of the local and dynamic properties of the catalytic sites, is still missing in the literature. Herein, we investigate the architectures and reactivity of the active centers of C₃N₄-supported SACs in a set of advanced *in situ* and *operando* techniques, unlocking key information on the reactivity of these materials.

2. Methods

We synthesized a series of Ni- and Cu-containing single-atom catalysts (SACs) in which metal atoms are uniformly dispersed on mesoporous graphitic C₃N₄. The characterization of these SACs involved a range of techniques, such as HRTEM, XPS, ICP-OES, CHN elemental analysis, surface area and porosity measurements, XRD, TEM, TGA, IR, and UV-Vis spectroscopy. FTIR measurements were performed with a Bruker Equinox 55 spectrophotometer equipped with a Globalbar source emitting radiation at infrared wavelengths, and spectra were collected both during an outgassing procedure at room temperature at preset time intervals, and after heat treatments at increasing temperatures (150-500 °C, 60 min). XAS measurements of Ni and Cu SACs were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. XAS spectra were acquired in fluorescence mode at Ni and Cu K-edges, 8333 and 8979 eV, respectively, under atmospheric conditions in terms of temperature and pressure. DFT calculations have been performed to rationalize and support the experimental evidence.

3. Results and discussion

The preliminary characterization *via* HRTEM, XPS, and XAS acquired under *ex situ* mode elucidated the initial state of the catalyst, which corresponded of highly dispersed metal sites. In this context, the hydrogenation of acetylene (C₂H₂) to ethene (C₂H₄) represents one of the most important reactions

catalyzed over metals and, as such, it has been thoroughly investigated as a model process for the characterization of metal catalysts and already studied by our group, also employing acetylene derivatives. Therefore, we took this hydrogenation process as a model reaction for more complex hydrogenation processes to understand the tendency of the single atoms to aggregate under reaction conditions. An *in situ* and *operando* XAS investigation in selected reducing and/or oxidizing atmosphere, and under hydrogenation conditions, was performed to clarify the conditions leading to the aggregation of metal atoms and how, instead, this can be prevented *via* modification of the surface of single-atom catalysts. The detailed *operando* XAS investigation provided crucial insights into the catalytic hydrogenation mechanisms governing isolated single atoms, shedding light on the intricate interplay of the oxidation state and metal coordination within the single-atom catalysts during the reaction. Furthermore, this study quantitatively delineated the impact of potential metal aggregation, demonstrating a 12% increase in oxidation state and a concurrent 8% reduction in metal coordination when such aggregation occurs.

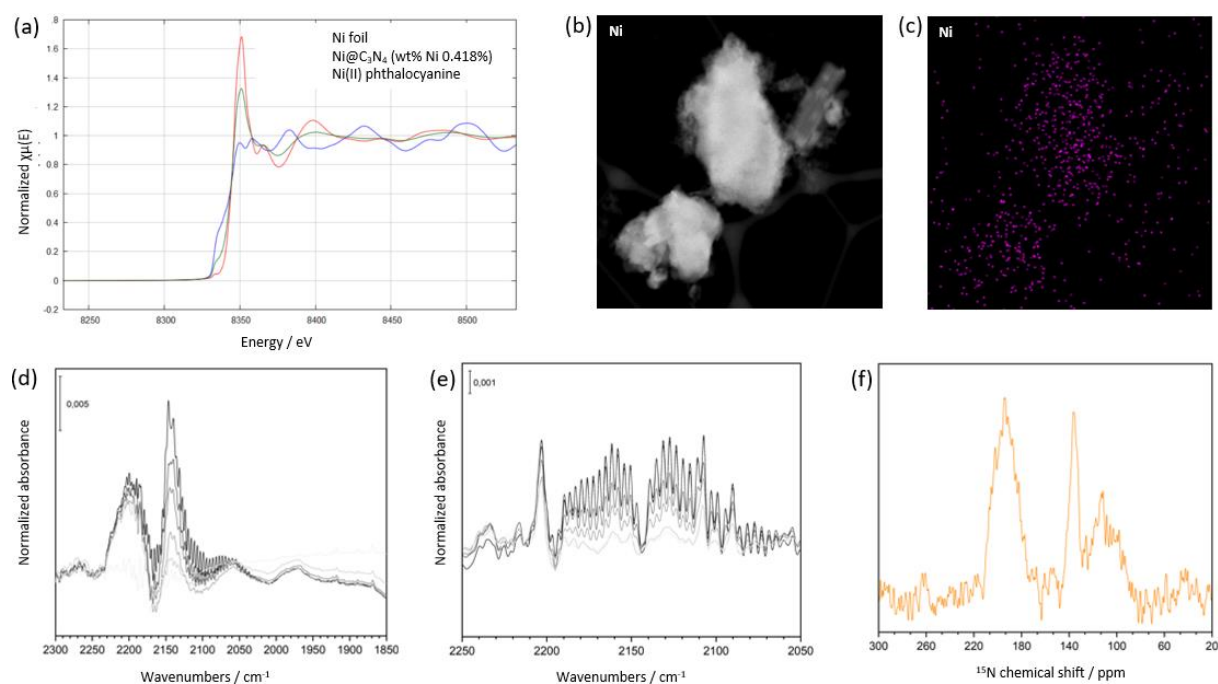


Figure 1. XANES spectra of Ni@C₃N₄ and reference materials (a), STEM of Ni@C₃N₄ (b), EDX of Ni@C₃N₄ (c), *operando* FTIR of Ni@C₃N₄ during hydrogenation (d,e), and ¹³C CP/MAS NMR spectra of Ni@C₃N₄ (f).

4. Conclusions

Our work sheds light on the structure and reactivity of carbon nitride-based single-atom catalysts during hydrogenation, paving at the same time new paths for a comprehensive elucidation of the local and dynamic structure of the active centers of these catalysts.

References

1. G. Vilé, G. Di Liberto, S. Tosoni, A. Sivo, V. Ruta, M. Nachtegaal, A. H. Clark, S. Agnoli, Y. Zou, A. Savateev, M. Antonietti, G. Pacchioni, *ACS Catal.* **2022**, *12*, 5.
2. M.A. Bajada, G. Di Liberto, S. Tosoni, V. Ruta, L. Mino, N. Allasia, A. Sivo, G. Pacchioni, G. Vilé, *Nature Synthesis*, **2023**, DOI 10.1038/s44160-023-00341-3.
3. G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. Lopez, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2015**, *54*, 11265-11269.

Keywords

Single-atom catalysts; Carbon nitride; *Operando* XAS; Hydrogenation.